

Honeycomb Weathering of Limestone Building on The Archaeological Sites on Leptis Magna (Libya): Causes, Processes and Damages.

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ABSTRACT

Honeycomb weathering is a common surface phenomenon affecting a variety of rocks in a range of environments. The processes involve the progressive of closely spaced cavities which are generally small with an average width few millimeters to several centimeters in diameter. Honeycomb weathering, also known as fretting, cavernous weathering, alveoli/alveolar weathering, stone lattice, stone lace or miniature tafoni weathering. Incipient honeycomb weathering in a homogeneous limestone has been experimentally reproduced by wind exposure and salt crystallization. It is a type of salt weathering common on coastal and semi-arid limestone. Honeycomb weathering occurs in many populated region and must have been noted in archaeological sites at Leptis Magna (Libya). Leptis Magna is a World Heritage site on the Mediterranean coast of North Africa in the Tripolitania region of Libya. In order to create an appropriated conservation concept, it was necessary to investigate the damage processes. For this purpose, X-ray powder diffraction (XRD), optical and scanning electron microscope (SEM) attached with EDX, Stereo microscope, polarizing microscopes (PM) were used. Biodeterioration problems in the site were analyzed taking into account their impact on the substrate and their relationship with environmental factors. Chemical analysis and field observations indicated that honeycomb weathering in coastal exposures of limestone at archaeological sites of the Leptis Magna results from evaporation of salt water

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deposited by wave splash from Mediterranean Sea. Microscopic examination of weathered samples show that erosion results from disaggregation of minerals grains rather than from chemical decomposition. Thin walls separating adjacent cavities seem to be due to protective effects of organic coatings produced by microscopic algae inhabiting the rock surface.

KEY WORDS: Honeycomb, Leptis Magna, Limestone, Environmental factors, Salts, Biodeterioration.

1. INTRODUCTION

Blocks of Leptis Magna/Labia stone, limestone of Lower Cretaceous age, display extensive honeycomb weathering features. Spatial variations in the degree of weathering, together with geochemical evidence, suggest that marine salt spray has played a key role in the development of the honeycombs. Leptis Magna is a World Heritage site on the Mediterranean coast of North Africa in the Tripolitania region of Libya. Its ruins are located in 3 km west of AlKhums, 12 km west of Villa Sileen, 80 km southeast of Misrata, 130 km east of Tripoli, on the coast where the Wadi Lebda meets the sea (fig.1a, b). The site is one of the most spectacular and unspoiled Roman ruins in the Mediterranean. It called Lpqqy, Neapolis, Lebida or Lebda to modern-day residents of Libya. Leptis Magna is added to the UNESCO World Heritage List, as one of 5 places in Libya. Originally founded by the Phoenicians in the 10th Century BC, it survived the attention of Spartan colonists, became a Punic city and eventually part of the new Roman province of Africa around 23 BC. Although it provided a source of building materials to various pillagers throughout history, it was not excavated until 1920. The number of great monuments of Leptis Magna makes it a bit difficult to point out highlights, but the theatre is clearly one, and it has a splendid view from its upper tiers ⁽¹⁾.

⁽¹⁾Bandineli, R. B., Caffarelli, E.V. and Caputo G.,(1964) The Buried City: Excavation at Leptis Magna, 1st edition, Weidenfeld and Nicolson, 1964, pg 17

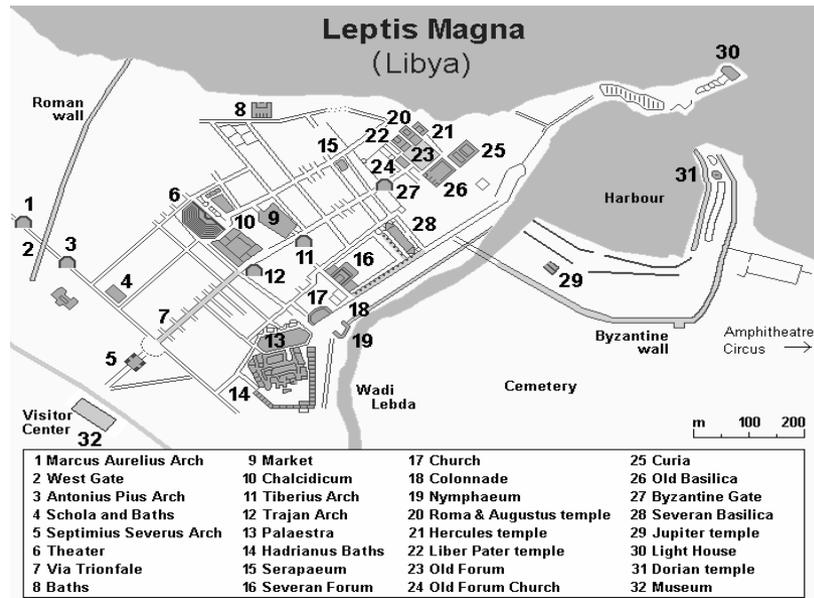


Fig. 1 Map of the main archaeological sites of Leptis Magna
wikipedia.org/wiki/File:LY-Leptis_Magna.png, 2010

The dryness of this location given its latitude and its maritime character are more typical of a Mediterranean climate. The temperature is moderate with a yearly average of 16°C; the extreme monthly means are 22°C (July) and 8°C (January). Nevertheless, maximum value of 46°C and minimum of 14°C have been recorded. The mean annual precipitation is 600 mm, and the average yearly relative humidity is 68%. There are 2350–2680 h of sunshine per year and no more than 12 frost days (table 1). The dominant wind directions are NW and SW (from the Mediterranean). Winds favour evaporation from stone surfaces and generation of marine aerosols. According to Auger ⁽²⁾, the marine influence on the alteration of monuments in this region extends as far as 100 km inland.

⁽²⁾ Auger F. (1987) Alteration des roches sous influence marine; degradation des pierres en oeuvre et simulation acceleree en laboratoire. These Doctorat d'Etat es Sciences. Universite de Poitiers, France, pp. 35-55.

Table (1) the weather average of Tripoli (wikipedia.org/wiki/Tripoli).

Month	Average sunlight hours	Temperature record		Discomfort from heat and humidity	Relative humidity		Average precipitation (mm)	Wet days (+025mm)
		Min	Max		am	pm		
Jan.	5	8	16	----	58	69	81	11
Feb.	6	9	17	-----	71	60	46	7
March.	6	11	19	-----	65	57	28	5
April	7	14	22	-----	62	57	10	2
May	8	16	24	Moderate	58	62	5	3
June	10	19	27	Medium	57	70	3	1
July	11	22	29	High	54	72	0	0.2
Aug.	11	22	39	High	72	69	0	0.3
Sept.	8	22	29	Medium	67	67	10	2
Oct.	7	18	27	Medium	65	59	41	5
Nov.	5	14	23	-----	66	53	66	7
Dec.	5	9	18	-----	65	55	94	11

Building materials of Leptis Magna;

Settlers from the Greek and Roman periods built cities of native limestone blocks excavated and cut to size. This is evident in the remains of cities such as Leptis-Magna, following this period of active building on a grand scale⁽³⁾. The Leptis Magna's building materials are made of local limestone from the location. The city was largely built out of local stone of varying grades from local sources. "Building was made considerably easier by the existence nearby (at Wadi Zennad as well as Lebda itself) of excellent quarries for stone and for a grey limestone that acquires a fine yellow patina with time. This quarry belonged to Al-Khumus formation. Al-Khumus formation was established by Mann for a sequence of about 70km of shallow marine limestone exposed near Al-Khumus, at this type locality. Al-Khumus formation consists of basal unit of Gypiferous marls with pelecypods, followed by siliceous, saccharoidal and marly limestone and calcareous clays. Acalcarenite horizon overlain by aconglomerate of disintegrated limestone pebbles marks the middle of the formation. The upper

⁽³⁾Rotherham, F., Spode, F., Elbah, S., & Fraser, D., (2003) A comparison of limestone quarries and their potential for restoration and after –use in Libya and the UK., proceedings of the 7th international conference of the international affiliation of land reclamationists runcorn/United Kingdome/13-16 May 2003, pp.331-340.

part contains fine grained algal and oolitic limestone and contains a marine Fauna of Foraminifera, Gastropodos, and Ostracods, which indicate suggest a Langhian age⁽⁴⁾. The stonework was finished with a lime mortar, which contains a high content of magnesium indicating a dolomitic limestone was used for burning the lime.

In the Leptis Magna, the honeycomb weathering is found on steep faces in the salt spray zone above the mean high tide level. The cavity development is initiated by salt weathering. In the intertidal zone, cavity shapes and sizes are primarily controlled by wetting/drying cycles, and the rate of development greatly diminishes when cavities reach a critical size where the amount of seawater left by receding tides is so great that evaporation no longer⁽⁵⁾. Honeycomb weathering commonly occurs in homogeneous sediments and massive crystalline rocks⁽⁶⁾. Honeycomb weathering is extensively developed on coastal building, although its distribution shows some variation according to local condition. Honeycomb weathering cavities can be found on building disperses through the intertidal zone, where they commonly consists of rather shallow circular depressions inhabited by a variety of marine organisms. The most spectacular occurrences of honeycomb weathering appear above the high tide line and occur approximately 2.5 m above mean tide level, Honeycomb weathering is most prominent in the zone extending up to about 3m above the high tide line, width of 5 to 10 cm although individual cavities sometimes reach diameter of more than 30cm. The diameter commonly exceeds the depth, which is seldom more than 10cm (fig.2). Shallow cavities are generally in the form of simple depressions, while deeper cavities typically widen toward the interior. Cavities generally occur within very restricted vertical range, and lithologically identical units at higher elevations do not

(4) Don Hallett,(2004) Petroleum geology of Libya, El-sevier ltd, London , pp.252-254

(⁵) Mustoe, G. E. (2010), Biogenic origin of coastal honeycomb weathering. Earth Surface Processes and Landforms, V.35, pp. 424:434.

(⁶) Mustoe, G. E., (1982), The original of honeycomb weathering, Society of America Bulletin, V. 93, pp. 108-115

contain honeycomb textures. In order to explain the observed differences in physical deterioration, samples of alveolar weathered limestone building were taken and analyzed on several locations of the archaeological sites at Leptis Magna (fig.3). The aim of the investigation was to understand the weathering processes which are the precondition for an appropriate conservation and restoration concept.



Fig. 2 **a** honeycomb weathering at the Leptis Magna **b** honeycomb weathering developed along inclined bedding in limestone at Leptis Magna **c** honeycomb weathering in homogenous limestone at Leptis Magna.

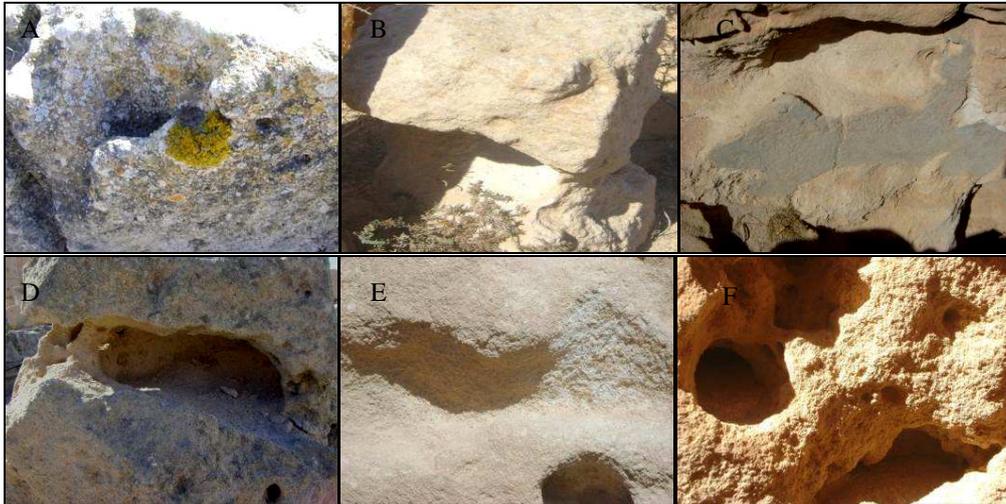


Fig. 3a:f shows pockets, caves and cavities resulted from weathering of limestone at Leptis Magna.

2. MATERIAL & METHODS

Samples were taken from the archaeological sites of the Leptis Magna. The following analytical techniques and scientific methods have been used to investigate all intrinsic and extrinsic

factors that have affected the archaeological sites weathering in order to define their deterioration mechanisms. Thin sections from the studied samples were prepared. The samples were first observed using Zies light optical microscope (LOM) to investigate surface of the samples and thin sections were examined using polarized transmitted microscopy Olympus BX41 attached with digital camera under 40-60X magnification in plane-polarized and crossed polarized-light. Megascopic features such as the fabric, general lithology, color, stratal boundaries, sedimentary structures, fossil content and other features were observed and recorded. Scanning electron microscope (SEM) investigation of the samples were carried out by the Jeol Jsm-5500 LV scanning electron microscope (JEOL, Japan) equipped with Oxford energy Dispersive X-ray Microanalyzer (EDX) system with link Isis software and model 6587 x-ray detector, Oxford, England). Various samples had been coated with gold (20nm). Stone samples and salt efflorescences were analysed from back-weathered expositions by using X-ray diffraction analysis using a diffractometer (Philips, PW 1840) with Ni-filtered Cu K α radiation at operating, conditions of 40 KV/25am and a scan speed of 2° (2 θ)/min. A study of biodeterioration of the Leptis Magna has been performed in order to characterize the kinds of bacteria and fungus. Depending on the conditions at the Leptis Magna, both heterotrophic and autotrophic microflora can be collected from the walls. Samples were collected by squashed and crumbed. For each sample, 1g was diluted with 9 ml of sterilized saline. Samples were shaken vigorously to form uniform solution of 10⁻¹ concentrations. The decimal serial dilutions (10⁻¹ to 10⁻⁵) were prepared using the method of Okafor N. & Ejiofor (1985)⁽⁷⁾. For the isolation of fungi, plate count method (Raper & Fennell, 1965)⁽⁸⁾ was used as follows: a known volume of the diluted sample, from sample serial dilutions, was used to

⁽⁷⁾ Okafor N., Ejiofor M.A.N., (1985) The linamarase of *Leuconostoc mesenteroides*, production, isolation and some properties. **J. Sci. Food Agric.**, 36:, pp 667-678.

⁽⁸⁾ Raper K.B., Fennell D.I., (1965) The Genus *Aspergillus*, Baltimore: Williams & Wilkins Company, pp 686 .

inoculate the used medium in plates. The plates contained Czapek's agar medium (Smith & Dawson, 1944)⁽⁹⁾ that was melted and kept at 45°C. The plates were incubated at 28°C for 5-7 days during which the developing fungi colonies were identified (Domsch et al., 1980)⁽¹⁰⁾. The same method was used for the isolation of bacteria, by using nutrient agar medium.

3. RESULTS

3.1 Petrographic Study:

The microscopic examination of the polished thin section of sample (W1) indicated that, the sample is composed of fossil fragments, micro spars, interaclsis embedded in micritic matrix and micro spary calcite cement stained by iron oxide (fig.4). According to Dunham's classification (1962)⁽¹¹⁾ the rock named as packstone. The microscopic examination of sample (W2) (fig.5) indicated that, the limestone sample consists essentially of bioclasts (fossil fragments), pelleds, and interaclsats embedded in micro spars and sparite cement with a biogenic texture. The rock name is grainstone, according to Dunham's. The thin section of sample (W3) revealed that, the rock consists of mainly of quartz, fossils, rock fragments and feldspars embedded in calcareous cement, as shown in (fig.6). The rock is packstone to grainstone according to Dunham's classification.

(9) Smith N.R., Dawson V.I., (1944) The bacteriostatic action of rose bengal in media used for plate count of soil fungi. Soil Sci., 58, pp. 467-471.

(10) Domsch K.H., Gams W., Anderson T.H., (1980) Compendium of Soil Fungi. Vol. 1-2. London: Academic Press.

(11) Dunham, R.J., (1962). Classification of carbonate rocks according to deposition texture. In: HAM, W.F.(ed): Classification of carbonate rocks, Tulsa akla-Am. Assac. Petrol. Geol. Publ., 1, pp. 108:121

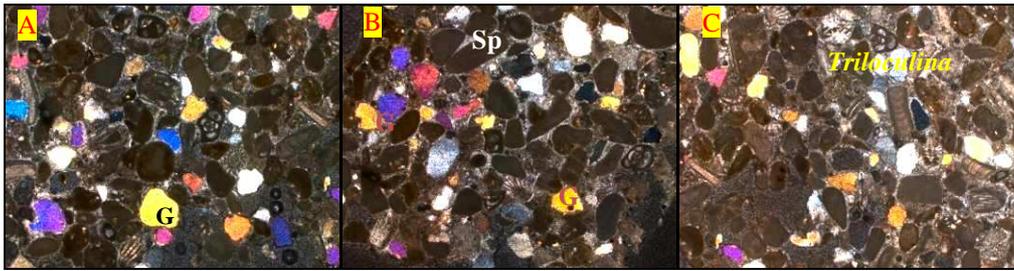


Fig. 4 a,b,c,d Petrographic view of limestone sample (W1) shows the components are fossil fragments, micro spar, micrite (low percent), interaclafts and iron oxide (X25).



Fig. 5a-c Petrographic view of limestone sample (W2) shows the weathered stone heterogeneous pore system contains ferric oxides and hydroxides (black spots) and shows the components are fossil fragments, structural less Peloids (SLP), quartz grains, structure peloids (SP) and iron oxide (X25).

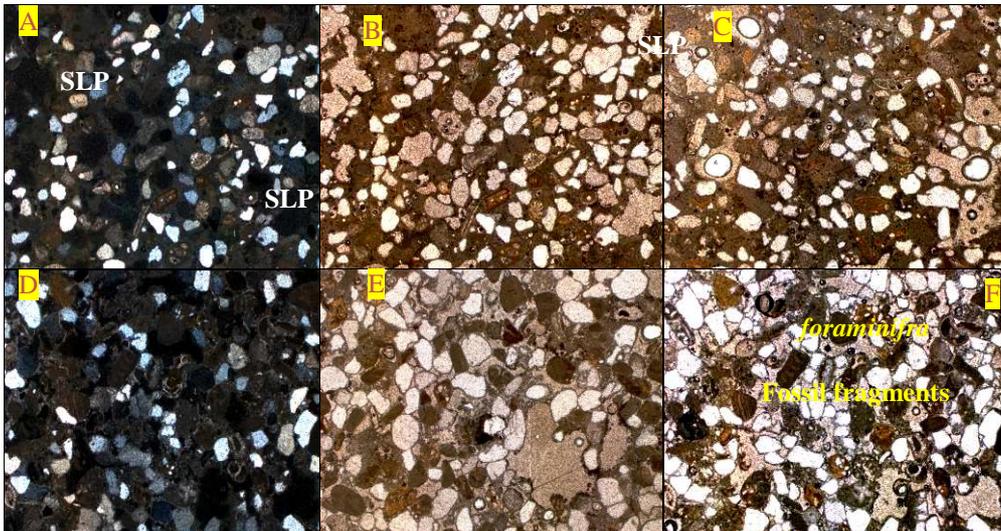


Fig. 6 (a,b,c,d) Petrographic view of limestone sample (W3) a,b,c show mineralogy is quartz, fossil fragments, rock fragments and feldspars d,e,f show fungal remains, and minor inertinite. Sporomorphs include *aunqueoloculua* sp., *milislida*(foraminifera), shell fragment(*prlecypoda*)

3.2 SEM TECHNIQUES AND EDX

SEM has been used for studying the morphological features of the same samples. The investigation captures show that there is wide range of deterioration features as shown in (Figure7) such as micro exfoliation, micro pitting appears clearly. Decayed limestone samples show etching features in some calcite and quartz grains indicating micro-dissolution processes (chemical weathering). Carbonate cement dissolution and subsequent calcite re-crystallisation are also observed. Drusy calcite sparite crystals are noticeable. Dissolution of cements occurs of the limestone which leads to an increasing in porosity and loss of cohesion of the stone. Crystal outlines are poorly defined as a consequence of leaching. Disintegration of calcite crystals is seen clearly and most of the ooides are removed due to the effect of soluble salts (figure8). The observations revealed significant presence of shell and shell fragments. Evidence of biophysical damage was observed in samples colonized by cyanobacterial and microalgal biofilms, Cyanobacterial filaments were observed to grow inside pores of the stone. Microalgae adhered closely to particles of the substratum, and grew inside preexisting pores and cracks (figure 9). Fungi are capable through a range of etching and chelating processes, to bore and burrow their way into mineral surfaces producing distinctive boreholes pits and channels. Anhedral and subhedral halite crystals of halite are found into the stones.

The EDX results (figure10) show that decayed samples contain Si, K, Ti, Mg, and Sr. The higher concentration of these elements is due to presence of clay minerals and Fe-oxi-hydroxides that make up the Curia micrite. Gavish & Friedman (1969)

mentioned that, magnesium, strontium and iron have to be analyzed because of their ability to substitute for calcium in the limestone and their expected variability with mineralogical changes by the weathering. The study showed Cl and high percentage of S. These elements are considered to form halite and gypsum.

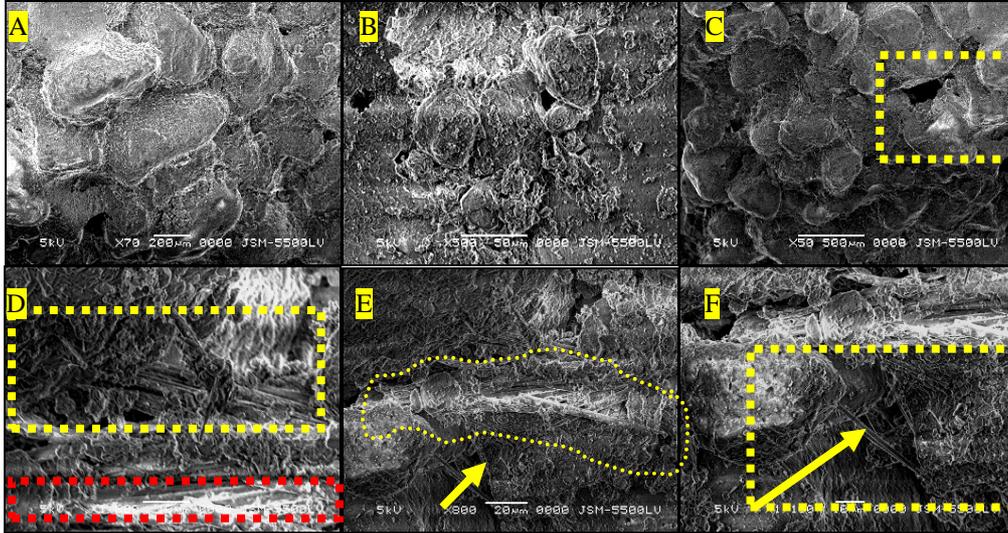


Fig. 7 a-f SEM-EDX microanalysis and photomograph of limestone sample(W1) **a** shows the ooids of oolitic **b** the Exfoliation of the calcite crystals **c** eroded pits **d** clay minerals &fungi hyphate **e,f** fungi hyphate.

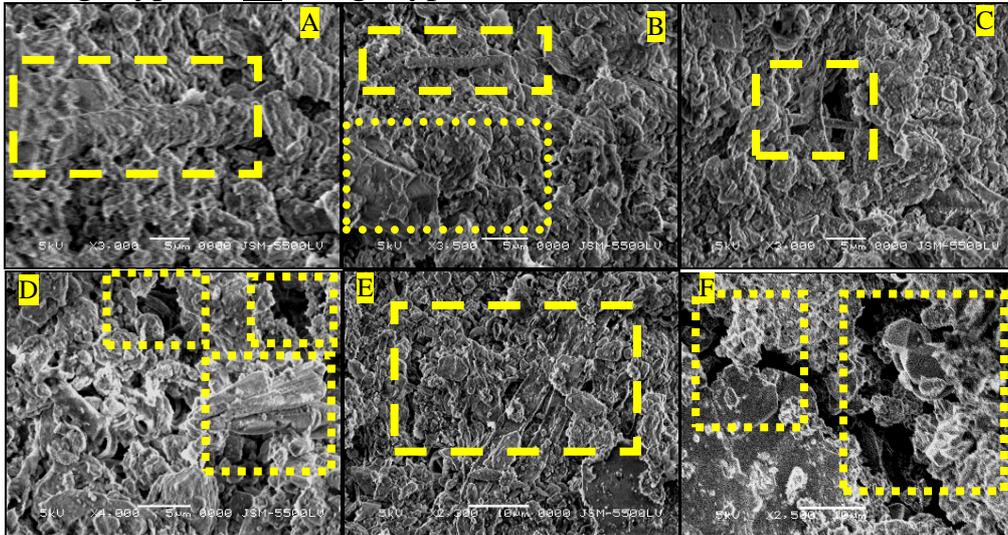


Fig.8 a-f SEM-EDX microanalysis and photomograph of limestone sample (W2) **a,b,c** fungi hyphate & eroodrd pits & halite crystals **d,e** clay minerals & eroodrd pits **f** Anhydral halite & gypsum.



Fig.9 a-f SEM-EDX microanalysis and photomograph of limestone sample (W3) **a** growth of mite (phylum: Arthropods) **b** the algal growth **d** Exfoliation and destroyed of the calcite ooids

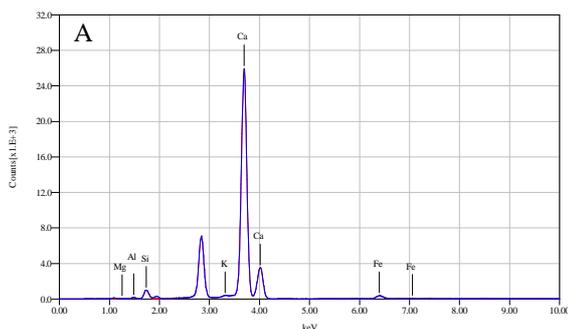
3.3. XRD Study:

Decayed stones have similar composition in different monuments and buildings with slight differences (tab. 4 and fig.10). Calcite is the major mineral in sites stones (90%) in Doric temple, quartz is present in trace amounts, gypsum appears in crusts in efflorescences, and in samples showing alveolar weathering, quartz is more abundant (15– 30%). In temple of Jupiter, decayed samples contain gypsum, halite, Biotite $\text{KMg}_3(\text{Si,Al})\text{O}_{10}(\text{OH})_2$, Forsterite (Mg_2SiO_4) and phyllosilicates. Curiously, halite is not detected in monuments and gypsum is only found in samples affected by flaking. The high content of sulphate is related to the atmosphere extremely polluted with SO_2 .

Table (4) XRD analytical results of limestone samples from Leptis Magna

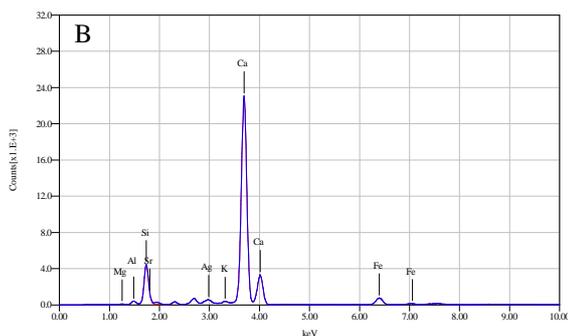
Samples	Analytical results		
	Major minerals	Minor minerals	Traces minerals
Sample A	Calcite (CaCO ₃)	Quartz, Halite	Forsterite(Mg ₂ SiO ₄)
Sample B	Calcite (CaCO ₃)	Quartz, Halite	Forsterite(Mg ₂ SiO ₄)
Sample C	Calcite (CaCO ₃)	Quartz, Halite	Forsterite(Mg ₂ SiO ₄)
Sample D	Calcite (CaCO ₃)	----- --	Quartz, Forsterite
Sample E	Calcite Quartz	& ----- --	Biotite KMg ₃ (Si,Al)O ₁₀ (OH) ₂
Sample F	Calcite	Quartz	Forsterite(Mg ₂ SiO ₄)
Sample G	Calcite &gypsum	Halite	Quartz

Table (1)



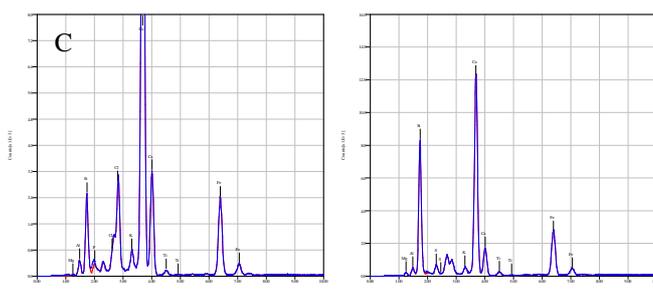
Elements	ms%	mol%
Mg	0.5296	0.8560
Al	1.1950	1.7404
Si	3.3083	4.6287
K	0.8772	0.8815
Ca	92.8102	90.993
Fe	1.2797	0.9004

Table (2)



Elements	ms%	mol%
Mg	1.5431	2.4530
Al	2.4488	3.5075
Si	12.2038	16.7928
S	1.2453	2.1324
K	1.2255	1.2113
Ca	75.3832	72.6883
Fe	2.0789	1.4386
Sr	0.9097	0.4013
Ag	4.2069	1.5073

Table (3)



Elements	ms%	mol%
Mg	0.6797	1.0823
Al	3.3960	4.8727
Si	7.9952	11.0208
P	0.6567	0.8208
Cl	0.7800	0.8517
K	2.1183	2.0973
Ca	75.7758	73.1936
Ti	0.8722	0.7049
Fe	7.7262	5.3559

Fig. 10 a-c SEM-EDX microanalysis of limestone samples **A** EDAX pattern and table 1 of the sample (W1) revealed the presence of Ca as a major elements, Si as a minor and Al, Mg, K as traces **B** EDX microanalysis pattern and table 2 of the sample (W2) revealed the presence of Ca & Si as a major elements, Al, Fe as a minor and S, Mg, Ag **C** EDAX pattern and table 3 of the sample (W3) revealed the presence of Ca & Si as a major elements, Al, Fe as a minor and Mg, P, Cl, Ti as traces.

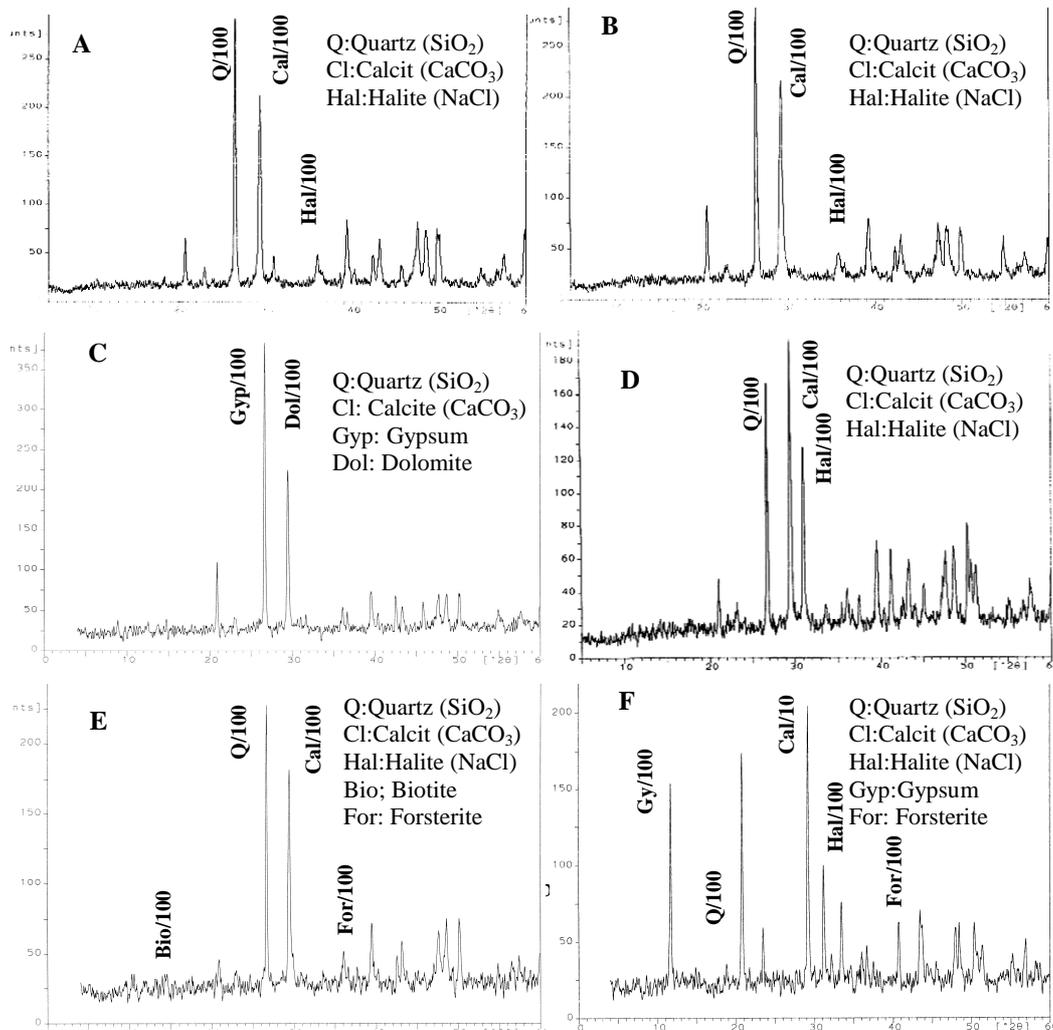


Fig. 11a-F XRD patterns of limestone and mortars of Leptis Magna

3.4. Light Optical Microscopes (LOM) Study

Optical (or light) microscopes are used to magnify small objects and can provide information about the structure and characteristics of a sample. Thin sections of stone can be studied to identify the mineral composition and its source. The investigation captures show that the limestone consists mainly of bioclats, pellets, intraclats and quartz embedded in sparite cement. The cement is stained in some parts by iron oxide. The rock shows texture rang

between clasts and bioclasts textured. The rock is packstone to grainstone according to Dunham's classification (figure12 a: i).

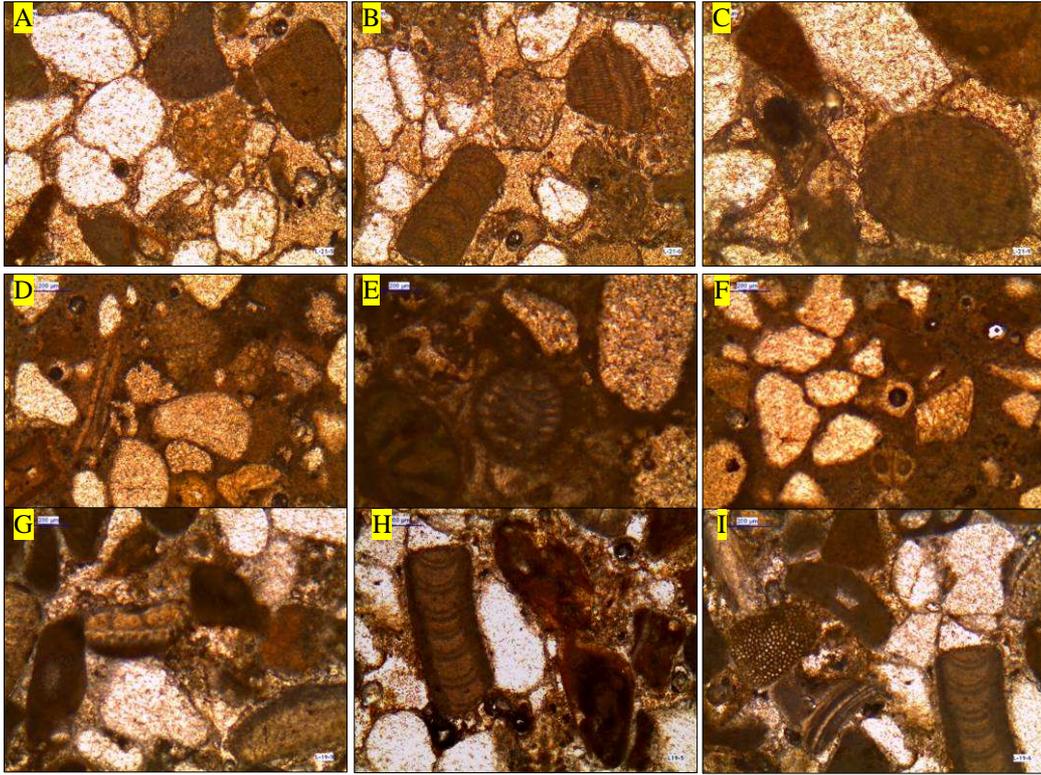


Fig.12 a:I micrograph of investigated samples by LOM Shows the component of limestone, bioclasts, pellets, intraclasts and quartz embedded in sparite cement.

3.5. Biological study results:

3.5. 1. Identification of microorganisms:

Identification of fungi was carried out on the basis of the macroscopic features of colonies, the morphological and structural characteristics according to (Domsch, 1980, Pinar, G. and Lubitz, W. ²⁰⁰²⁽¹²⁾). A light microscope with a magnification of 40× was used

(¹²) Pinar G., Lubitz, W., (2002) Molecular techniques application to the analysis of microbial communities colonizing. Art works and to the monitoring of changes. Case study: wall paintings of the castle of Herberstein, advanced course, 8-9 Nov., Florence.

for preliminary identification of the moulds to generic level. Light microscope with a magnification of 400× was used for preliminary identification of the fungi including (*Aspergillus niger*, *Aspergillus fumigates*, *St. Verruculosum*, *Alternaria alternate*, *Fusarium moniliforma*).

Identification of bacteria: For identification of bacterial isolates from Leptis Magna, the results showed that identified bacteria included (*Pseudomonas sp.*, *Clostridium sp.*, *Pseudomonas sp.*, *Bacillus cereus*, *Bacillus pumilus*, *Staphylococcus sp.*) as shown in (fig. 13).

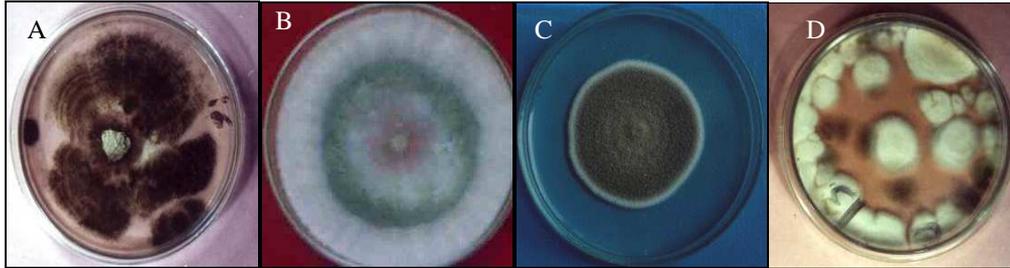


Fig. 13a:d the identified fungus from some archaeological sites at Leptis Magna.

4. DISCUSSION

Considering the observations on-site together with analysis it is possible to explain the processes of alveolar weathering at Leptis-Magna. In this part of the study all destruction factors dominating in the study area and the main components of weathering phenomena "mechanism and resulted forms" have been observed, studied and explained. There is consensus in the literature that the relative importance of physical and chemical weathering processes for alveoli to develop is related to lithology and structure of rocks, and topographical and environmental conditions. Therefore, alveolar weathering can only be satisfactory explained by invoking the synergism of a range of weathering mechanisms.

The results from optical microscopy and SEM show that weathering in Leptis Magna takes place through the following combined chemical and physical processes which lead to granular disaggregation and ultimately to alveolar weathering: cement

dissolution, chemical decomposition and physical action of salt crystallization. The SEM observations show also that salts are found deeper in the studied samples. Chemically weathered quartz grains have been described ⁽¹³⁾, and it is established that silica dissolution is enhanced under saline conditions (e.g. by sodium chloride) ⁽¹⁴⁾. Considering the above mentioned, it is suggested that the etching features observed in some quartz grains can be due to the effect of salt loading from sea spray. The petrographic characteristics of decayed stones indicated that cement dissolution is due to the action of sea-salt spray. The ionic strength of the saline solution that wets the stones under direct exposure to salt spray effect should increase the dissolution of the cement ⁽¹⁵⁾. The carbonate cement dissolution leads to a well-connected porous network, and as a consequence, favours an increment of the total porosity. This allows a deeper capillary migration of solutions towards the interior of the stone. The concept that honeycomb weathering results from physical action of salt crystallization was first advanced by Hume(1925)⁽¹⁶⁾, who observed masses of fibrous salt crystals associated with honeycomb structures in nodular limestone of the Ma'aza plateau east of the Nile river in Egypt. Salts may be introduced by migration in fluids or from salts contained within the original sediment. Salt crystallization, otherwise known as haloclasty, causes disintegration of stone when saline solutions seep into cracks and joints in the rocks and evaporate, leaving salt crystals behind. These salt crystals expand as they are heated up, exerting pressure on the confining rock. Salt crystallization may also take place when solutions decompose limestone to form salt

⁽¹³⁾ Young A.R.M) 1987)Salt as an agent in the development of cavernous weathering. Geology; 15:962 –6.

⁽¹⁴⁾Young A.R.M(1987), op.cit p.6

⁽¹⁵⁾ Cardell C, Rivas T, Mosquera MJ, Birginie JM, Moropoulou A, Prieto B, Silva B, Van Grieken R. (2002) Patterns of damage in igneous and sedimentary rocks under conditions simulating sea-salt weathering. Earth Surf Processes Landform, in press.

⁽¹⁶⁾ Hume, W. F., (1925), Geology of Egypt, v.1, Surface features: Cairo, Government press, pp. 214-216.

solutions of sodium chloride of which the moisture evaporates to form their respective salt crystals. These salts can expand up to three times or even more. It is normally associated with arid climates where strong heating causes strong evaporation and therefore salt crystallization. It is also common along coasts. An example of salt weathering can be seen in the honeycombed stones in sea wall. Different results obtained of mineralogical composition study by XRD completely agree with others obtained by XRF.

Our field observations reveal that honeycomb weathering at Leptis Magna buildings are due to surrounding environment of the building. To form a solution, it is necessary to have a water source other than rainwater, which leaches salts from the stone surface. Water vapour proceeds from sea-spray droplets, whose input has been confirmed by the enrichment factors ⁽¹⁷⁾. Condensation phenomenon can also wet stone surfaces. Then, a brine solution has to be formed and, before drying, has to wet the stone surface long enough to migrate towards inside the stone ⁽¹⁸⁾. High relative humidity like the ones reported in the Leptis Magna (e.g. average yearly RH75%), and variation of the relative humidity through 75% (the equilibrium relative humidity for NaCl at 25°C is 75.03%) may allow solution formation. Thus, for relative humidity) 75%, water fixation led to dissolution of salts present in the stones. The solution penetration is determined by the pore network. Moisture must be present to allow for the salt to settle on the rocks, so that as the salt solution evaporates as variation on humidity and temperature, the salt begins to crystallize within the pore-spaces of the rock. Porous rock is also needed so that there are pore-spaces for the salt to crystallize within. These salt crystals pry apart the mineral grains leaving them vulnerable to other forms of weathering. It seems that this local supersaturation and subsequent buildup of salt

⁽¹⁷⁾Cardell C., Delalieux F., Roumpopoulo K., A. Moropoulou, F. Augerc, Van Grieken, R. (2003) Salt-induced decay in calcareous stone monuments and buildings in a marine environment in SW France, *Construction and Building Materials* 17, pp.165–179

⁽¹⁸⁾De Freitas VP, Abrantes V, Crausse P. (1996) Moisture migration in building walls. *Analysis of the interface phenomena. Build Environ*; 31(2): pp.99 –108.

crystallization pressure ultimately result in the formation of honeycomb features. (Mustoe, G. E., 1982)⁽¹⁹⁾. The hydrostatic pressure generated by salt crystallization disintegrates the stone. Salt-induced decay of porous, granular oolitic limestone is often manifested initially by contour scaling followed by retreatment of the rapid surface through granular disintegration and/or multiple flaking (Smith et al. 2003)⁽²⁰⁾.

Wind action is invoked for alveoli to develop in Leptis Magna stone. Buildings exposed to overall winds "The dominant wind directions are NW and SW (from the Mediterranean)". Honeycomb weathering is a type of salt weathering common on coastal and semi-arid limestone. It has experimentally resulted from a dynamic balance between the corrosive action of salt crystallization and wind exposure (Mustoe, 1982)⁽²¹⁾. Wind action is reported in the literature as a key factor for the formation of alveolar weathering. Heterogeneous wind which flow over a stone surface is important in the development of this weathering pattern. Wind promotes evaporative salt growth between grains on a stone surface, resulting in the development of small, randomly distributed cavities. A reduction in air pressure within the cavities results in increased wind speed and rapid evaporation. High evaporation rate and evaporative cooling of the saline solution in the cavity lead to more rapid and greater granular disintegration than in the surrounding areas. It seems that this local supersaturation and subsequent buildup of salt crystallization pressure ultimately result in the formation of honeycomb features. For the first time, these experimental results demonstrate the close relationship between salts, wind, and honeycomb weathering. They also offer new ways to understand the genesis of this striking and sometimes harmful

⁽¹⁹⁾Mustoe, G. E. op. cit. pp. 108-115

⁽²⁰⁾ Smith, B.J., Torok, A., McAlister, J.J. and Megarry, Y.(2003), Observations on the factors influencing stability of building stones following contour scaling: a case study of oolitic limestone from Budapest, Hungary. *Building and Environment* , n.38, pp.1173–1183.

⁽²¹⁾Mustoe, G. E. The Origin of Honeycomb Weathering, Geological Society of America Bulletin, 1982, V. 93, pp. 108-115.

weathering pattern⁽²²⁾. Wind action is essential for removing debris from the interior of the cavities, which in the current area can be done by marine breezes, such that alveolar weathering is known to be a self-propagating process⁽²³⁾. Short-term fluctuation of temperatures in Leptis Magna stone surface can be achieved in the current area in response to variations in wind-speed and cloud cover, and may ultimately contribute to stone breakdown through 'fatigue' effects.

The optical and electronic microscopy reveals that the presence of fungi hyphate and algal and the microbiological study identified several kinds of fungus including (*Aspergillus niger*, *Aspergillus fumigates*, *St. Verruculosum*, *Alternaria altern;ate*, *Fusarium moniliforma*) and several kinds of bacteria including (*Pseudomonas sp.*, *Clostridium sp.*, *Bacillus cereus*, *Bacillus pumilus*, *Staphylococcus sp.*).

Honeycomb weathering results from a dynamic balance between the corrosive action of salt and the protective effects of endolithic microbes. Cavity patterns produced by complex interactions between inorganic processes and biologic activity provide a geological model of 'self-organization'⁽²⁴⁾. Biodeteriogen is an organism that is capable of causing biodeterioration. A wide variety of biodeteriogens have been identified on stone monuments in tropical environments due to the particularly favorable environmental conditions (high relative humidity, high temperatures, and heavy rainfall) in those regions. These organisms can cause direct or indirect damage to many kinds of stone. In some cases, the ability to cause serious damage has been well established; in others, it remains conjectural. Biophysical deterioration of stone may occur due to pressure exerted on the surrounding surface

⁽²²⁾Rodriguez, C. N., Doehne E., Sebastian E., 1999, Origins of honeycomb weathering: The role of salts and wind, GSA Bulletin, V. 111, NO. 8, pp. 1250-1255.

⁽²³⁾Dorn RI. Digital (1995) Processing of backscatter electron imagery: a microscopic approach to quantifying chemical weathering. Geol Soc Am Bull; 107:725-41.

⁽²⁴⁾Mustoe, G. E., (1982), The Origin of Honeycomb Weathering, Geological Society of America Bulletin, v. 93, p. 108-115.

material during the growth or movement of an organism or its parts, such as hyphae and extensive root systems, penetrate deeply into the stone through preexisting cracks or crevices, causing stresses that lead to physical damage of surrounding stone material (Kumar R. & Anuradha V.K. 1999)⁽²⁵⁾. Biochemical deterioration resulting from assimilatory processes, where the organism uses the stone surface as a source of nutrition, is probably more easily understood than deterioration resulting from dissimilatory processes, where the organism produces a variety of metabolites that react chemically with the stone surface (Jain, Mishra, and Singh 1993)⁽²⁶⁾. Most autotrophic microorganisms produce acids that can attack and dissolve some types of stone as *Pseudomonas sp.*, (Autotrophic nitrifying bacteria) which can play an important role in degradation by oxidizing ammonia to nitrite and nitrate ions, which may result in nitric acid formation. Stone dissolution, powdering, and formation of soluble nitrate salts that appear as efflorescence on the stone surface are processes that have all been demonstrated experimentally (Jain, Saxena, and Singh 1991)⁽²⁷⁾. Heterotrophic organisms as *Clostridium sp.* also produce organic acids that are capable of dissolving minerals of stone with the leaching of cations. Inorganic and organic acids decompose stone minerals by producing salts and chelates. An increased volume of soluble salts or chelates may also cause stresses in the pores, resulting in the formation of cracks (Saxena, Jain, and Singh 1991)⁽²⁸⁾.

⁽²⁵⁾Kumar, R., Anuradha V.K., Biodeterioration of stone in tropical environments, Paul Getty trust , printed in the USA, 1999.

⁽²⁶⁾Jain, K. K., A. K. Mishra, and T. Singh. Biodeterioration of stone: A review of mechanism involved. In Recent Advances in Biodeterioration and Biodegradation, vol.1, Calcutta: Naya Prokash. 1993, pp 323-354.

⁽²⁷⁾Saxena, V. K., K. K. Jain, and. Singh T. Mechanisms of biologically induced damage to stone materials. In Biodeterioration of Cultural Property: Proceedings of the International Conference on Biodeterioration of cultural property, Held at national Research Laboratory for Conservation of Cultural Property, in Collaboration with ICCROM and INTACH. New Delhi: Macmillan India. 1991. pp.249-258. Saxena, V. K., K. K. Jain, and. Singh T., op cit., pp. 249-258.

⁽²⁸⁾Saxena, V. K., K. K. Jain, and. Singh T., ibid., pp. 249-258.

Limestone at Leptis Magna exposed to the weathering effects of the ocean are dissolved and eroded to make a fascinating landscape east of Tripoli Libya. Weathering of limestone involves carbon dioxide and water. Carbon dioxide dissolved in water provides ions that produce free hydrogen. Carbon dioxide in the atmosphere combines with water to form carbonic acid (H_2CO_3): $H_2O + CO_2 \rightarrow H_2CO_3$ though weak, when carbonic acid is combined with a mineral like calcite ($CaCO_3$), an important part of limestone, calcium and bicarbonate ions are removed causing the rock to erode away. The uneven effects of this process create pockets, caves, and crevices seen in the figure 3. Granular disintegration was attributed to chemical alteration along grain surface, swelling and shrinking of interstitial clay (Fred G. Bell 1999)⁽²⁹⁾. The solution in limestone occurred as a result of carbon dioxide that is dissolved in the rainwater producing weak carbonic acid in unpolluted environments which reacts with calcium carbonate (the limestone) and forms calcium bicarbonate. This process speeds up with a decrease in temperature. That plays a very important role in transformation of carbonaceous building stones component into bicarbonate which dissolves slowly (Rodriguez, C. et al 1999)⁽³⁰⁾.

CONCLUSION:

- Blocks of Leptis Magna/Labia stone, limestone of Lower Cretaceous age, display extensive honeycomb weathering features. Spatial variations in the degree of weathering, together with geochemical evidence, suggest that marine salt spray has played a key role in the development of the honeycombs.
- The principal weathering mechanics involved is granular disintegration and micro de-lamination induced by chemical

⁽²⁹⁾ Fred G.B. Karst and cavernous rocks In Engineering And Construction, M.G. Culshaw, Tony Waltham, 1999

⁽³⁰⁾ Rodriguez, C., Navarro, Doehne, E., and Sebastian, E., Origins of honeycomb weathering, the role of salts and wind, GSA Bulletin, August 1999, v. 111, no. 8, pp. 1250-1255

alteration along inter-grain boundaries and differential swelling and contraction of clays within the rock.

- Salt crystallization and hydration pressures within the rock pores appear to have played a minor role in this case.
- Honeycomb weathering results from a dynamic balance between the corrosive action of salt and the protective effects of endolithic microbes. Cavity patterns produced by complex interactions between inorganic processes and biologic activity.

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